# Multifunctional catalysts of three-dimensionally ordered macroporous oxide-supported Au@Pt core–shell nanoparticles with high catalytic activity and stability for soot oxidation

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Yuechang Wei [a], Zhen Zhao [a,*], Jian Liu [a], Shetian Liu [b], Chunming Xu [a,*], Aijun Duan [a], Guiyuan Jiang [a]

[a] State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China
[b] Coal Chemical Catalyst Center, National Institute of Clean-and-Low-Carbon Energy, Beijing, China

## ABSTRACT

Supported Au@Pt core–shell nanoparticles (NPs) were successfully synthesized on three-dimensionally ordered macroporous (3DOM) oxides by a one-step gas bubbling-assisted membrane reduction (GBMR) method. The Au@Pt core–shell NPs were highly dispersed on the pore wall of oxides and the Pt shell was obtained by direct epitaxial overgrowth on the surface of the Au core. The multifunctional nanocatalysts were used for diesel soot oxidation. 3DOM structure facilitates the contact between soot particles and catalysts, and the synergetic effect of the Au core and Pt shell significantly increases the surface concentration of active $O_2^-$ species. 3DOM $Ce_{0.8}Zr_{0.2}O_2$-supported Au@Pt core–shell NP catalyst is one of the best catalysts reported so far for soot oxidation under "loose" contact between soot and catalyst. The stability of the Au-based catalysts for soot oxidation is also improved due to the formation of an Au@Pt core–shell structure.

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## 1. Introduction

Particulate matters (PM, mainly containing soot) emitted from diesel engines have caused acute human health and environmental problems [1]. A wall-flow filter is normally employed to trap the soot particulates. However, to keep the back pressure of the engine low, the filter needs frequent regeneration by burning the trapped soot at high temperatures, which often damage the filter. A self-generable soot particulate filter (SSF) is thus needed to reduce the soot emission. The key challenge of the SSF technology is to develop a catalyst that can catalyze soot oxidation at low temperatures as much as possible [2–4]. Catalytic oxidation of soot is a kind of deep oxidation that takes place at a three-phase boundary of a solid catalyst, a solid reactant (soot), and gaseous reactants ($O_2$, NO) [5–7]. Thus, the catalytic activity of a material for diesel soot oxidation is affected by two factors: the contact efficiency between solid soot particles and the catalyst surface, and the intrinsic activity of the catalyst [8–15]. Literature studies have revealed that three-dimensionally ordered macroporous (3DOM) oxides with large pore size (>50 nm) [16–18] remarkably improve the catalytic activity for diesel soot oxidation due to the increased

contact efficiency between 3DOM oxide and a solid reactant [19,20]. Supported gold nanoparticles (NPs) as active components are an attractive choice to enhance the intrinsic catalytic performance of 3DOM metal oxides, because supported Au NPs are able to promote adsorption–activation of molecule oxygen and increase the amount of active oxygen species ($O_2^{\&-}$) on the catalyst surface [21–26]. Unfortunately, the thermal stability of supported Au-based catalysts for soot oxidation is poor [24–26]. Improving the stability and catalytic activity of 3DOM oxides-supported Au-based catalysts for soot oxidation is therefore the key issue in the development of relevant catalysts.

Combining Au with other metals to form bi- or multimetallic nanostructures could be an efficient way to tune the atomic-scale characteristics and the catalytic activity of the supported Au NPs [27,28]. Surface science studies have shown that a creation of hetero-(metal–metal) bonds in a well-defined Au surface may induce significant changes in the electronic structure and catalytic properties of supported Au NPs [29,30]. Bimetallic core–shell Au@Metal NPs with controlled shapes on a support have become increasingly important, providing attractive perspectives for effectively tuning the functionalities of Au nanocrystals [31]. Among all of the metal active components, Pt is one of the most suitable elements for the shell layer metal on the Au core, because the Pt shell not only improves the thermal stability of the Au core, but also optimizes

the utilization of the Pt component, which is desired in many important commercial catalysts for chemical processes, especially catalysts for automotive exhaust cleaning [32]. Currently, supported Au@Pt core–shell NP materials have attracted considerable attention, and they show superior catalytic properties unattainable by their monometallic counterparts and alloys [33]. Therefore, the design and synthesis of supported Au@Pt core–shell NPs deposited on the surfaces of 3DOM oxides not only is a potential route to enhance their catalytic activities and stability for soot oxidation, but also has an economic benefit in the reduced amount of noble metals (Pt and Au) required.

The nanometer and atomic-scale characteristics of fabricated functional nanostructure materials play a central role in heterogeneous catalytic reactions [34,35]. To rationalize the extreme dependence of the catalytic activity on the structure and size of the Au@Pt nanoparticles, the nanostructure of the Pt shell should be effectively controlled. In the structure-sensitive heterogeneous catalytic reactions, tailored Au@Pt core–shell NPs with an ideal Pt shell thickness and narrow particle size distribution are especially vital. Conventional methods for the synthesis of Au@Pt core–shell structured NPs includes at least two steps, i.e., a two-step seed-mediated growth method via sequential complexation and chemical reduction of, first, the core metal and, second, the shell [36,37]. But facile one-step synthesis of oxides-supported core–shell-structured Au@Pt NPs is rarely reported, especially the synthesis of Au@Pt NPs on the surfaces of nanostructure-3DOM supports [38]. Hence, the facile synthesis of supported Au@Pt NPs on the surfaces of 3DOM oxides is a primary goal of catalyst design and is still a great challenge.

Here, we first report a simple one-step route for the synthesis of Pt-on-Au NPs on the surface of 3DOM $Ce_{0.8}Zr_{0.2}O_2$ supports via a gas-bubbling-assisted membrane reduction (GBMR) method. This technique uses $NaBH_4$ as the reducing reagent, and the addition rate and dispersion of $NaBH_4$ solution are strictly controlled. It may be a practical way to regulate the nucleation process to produce a mass of metal–metal core–shell nanocrystals over oxide supports [39]. We carried out a diesel soot oxidation reaction to explore the high catalytic activity and stability of 3DOM oxides-supported Au@Pt core–shell NP catalysts. The well-defined 3DOM structures consisting of interconnected networks of spherical voids with large pore size (>50 nm) are favorable for improving contact between catalysts and solid soot particulates. And the dendritic Pt shell on the surface of the Au core could be beneficial for increasing the surface concentration of active oxygen species ($O_2^{\delta-}$: $O_2^-$ and $O_2^{2-}$) and improving the stability of the Au core. We believe that the synthesis method is scientifically and technologically important for the creation of novel supported core–shell nanoarchitectures with designed compositions and desired functions, and the multifunctional material of 3DOM oxides-supported Au@Pt core–shell NPs is an excellent system for catalytic reactions or surface chemical processes that occur at the interfaces of reactant and catalyst.

## 2. Experimental section

### 2.1. Preparation of materials

#### 2.1.1. Synthesis of 3DOM oxide support

Syntheses of monodispersed polymethyl methacrylate (PMMA) microspheres, assembly of templates, and preparation of 3DOM $Ce_{0.8}Zr_{0.2}O_2$ supports by a colloidal crystal template (CCT) method are similar to that described previously [24]. The typical schematic is shown in Fig. S1. The dried sample was calcined to remove the CCT in an air flow of 80 ml min$^{-1}$ in a tube furnace. The sample temperature was raised at 1 °C min$^{-1}$ from room temperature to

550 °C and kept at 550 °C for 5 h. Finally, 3DOM $Ce_{0.8}Zr_{0.2}O_2$ support was obtained. The 3DOM $Ce_{0.8}Zr_{0.2}O_2$ support is named 3DOM CZO. The preparation processes of PMMA and 3DOM $Ce_{0.8}Zr_{0.2}O_2$ support are shown in detail in the Experimental Section of the Electronic Supplementary Information.

#### 2.1.2. Synthesis of 3DOM CZO-supported Au@Pt core–shell NP catalysts

3DOM $Au_n@Pt_m$/CZO catalysts, where $n$ and $m$ are the nominal weight percentages of Au and Pt in catalysts, i.e., $n$ wt% and $m$ wt%, respectively, were synthesized via the GBMR method just developed in our our lab [24–26]. Detailed information about the experimental apparatus is shown in Figs. S2 and S3 and the reagent specifications are shown in Table S1. The typical preparation procedures were described as follows: Poly N-vinyl-2-pyrrolidone (PVP) solution as a stabilizer was added into the mixed solution (100 ml) of $HAuCl_4$ and $H_2PtCl_6$ (Beaker I). The 3DOM CZO support was then introduced into the solution. The mixture solution was driven to form a cycling flow between the membrane reactor and Beaker I by a peristaltic pump at a flow rate of ~360 ml min$^{-1}$. The metal precursor solution flowed in the glass tube reactor and outside the ceramic tubes. The hydrogen gas was also injected into the membrane reactor with two ceramic membrane tubes ($\varnothing$ 3 mm × 160 mm). Meanwhile, the reductant solution ($NaBH_4$) (50 ml) was injected into the membrane reactor with the two other membrane tubes by pump at a constant flow of 0.2 ml min$^{-1}$. The $NaBH_4$ solution was infiltrated through the abundant holes ($d$ = 40 nm) on the walls of the ceramic tubes into the glass tube reactor, where the reduction of metal ions occurred immediately when the two solutions met. The molar ratio of noble metal cations to $NaBH_4$ was about 1:5. The hydrogen-bubbling-assisted stirring operation (40 ml min$^{-1}$) was developed to vigorously stir the solution. The synthesis process stopped after all the $NaBH_4$ in the solution was consumed. The reaction system was further vigorously bubbled with hydrogen gas for 1 h and subsequently kept static for 1 h. The product was then filtered and washed with distilled water at 60 °C until no Cl$^-$ was detected with an $AgNO_3$ test. In order to keep the structural stability of the catalysts and remove the $H_2O$ and stability reagent, the final products were calcined in a furnace at 500 °C for 0.5 h and the desired 3DOM $Au_n@Pt_m$/CZO catalysts were obtained.

For one-step synthesis of supported Au@Pt core–shell nanoparticles on the surface of 3DOM CZO via a GBMR method, the flow rate of the reductant solution is the key factor for Au@Pt core–shell structure. In order to verify the role of the flow rate of the reductant solution, the experiment was carried out under a flow rate of 2.0 ml min$^{-1}$, and 3DOM CZO-supported Au–Pt alloy nanoparticles were obtained.

### 2.2. Characterization

The scanning electron microscope (SEM) observations were carried out on a FEI Quanta 200F instrument using an accelerating voltage of 5 kV.

The transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) images were taken using a JEOL JEM 2100 electron microscope equipped with a field emission source at an accelerating voltage of 200 kV. The average particle diameter was calculated from the mean diameter frequency distribution with the formula $d = \sum n_i d_i / \sum n_i$, where $n_i$ is the number of particles with particle diameter ($d_i$) in a certain range.

High-angle annular dark field (HAADF) images in scanning transmission electron microscope (STEM) mode and energy-dispersive X-ray spectroscopy (EDX) analyses were also carried